Organosolv delignification of steam exploded wheat straw

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Abstract: *It has been increasing the interest in the study of alternative pulping processes that conciliate high performance and protection to the environment. In the same way, the use of agricultural residues has been more and more reminded as promising raw material for production of chemical products. The wheat straw is a very abundant agricultural residue and it has been used in many countries for the production of cellulosic pulps. This work describes the effect of the pretreatment by steam explosion on the acetone-water pulping of wheat straw. The samples of wheat straw were treated by steam explosion at 190 and 210^oC for 4 min and later submitted to the treatment with acetone-water (1:1,v:v) at different temperatures (140, 160 and 200^oC) and 60 min as reaction times. The pretreatment led to an increase in the amount of extracted lignin in the organosolv pulping. This effect was more pronounced in the pulping performed at lower temperatures. The use of higher temperatures in the treatment by steam explosion was more significant as shown by lower pulp yield and higher delignification extent.*

Key words: *Wheat straw, steam explosion, delignification*

Resumo: *Atualmente tem-se aumentado o interesse no estudo de processos alternativos de polpação que conciliam um alto desempenho e causando pouco impacto ambiental. Da mesma maneira, o uso de resíduos agrícolas é cada vez mais citado como matéria-prima promissora para produção de produtos químicos. A palha de trigo é um resíduo agrícola muito abundante e foi usado em muitos países para a produção de polpas de celulose. Este trabalho descreve o efeito do pré-tratamento através de uma explosão a vapor seguido de uma polpação com acetona/água na palha de trigo. As amostras de palha de trigo foram tratadas através de* *explosão a vapor com temperaturas variando entre 190 e 210^{o}C durante 4 min e em seguida submetidas ao tratamento com acetona/água (1:1/v:v) a diferentes temperaturas (140, 160 e 200^{o}C) durante um tempo de 60 min de polpação. O pré-tratamento por explosão a vapor levou a um aumento da quantidade de lignina extraída pela polpação organossolve. Este efeito foi mais pronunciado para as polpações realizadas a menores temperaturas. O uso de temperaturas mais elevadas no tratamento por explosão a vapor foi mais significativo, pois resultou em menores valores de rendimento de polpa e maiores taxas de deslignificação.*

Palavras chaves: *Palha de trigo, explosão a vapor, deslignificação*

1. Introduction

The utilization of wood as raw material for pulp production is restricted in several countries due to forest resources limitations. In this situation and even when the wood supply is abundant, the utilization of fast growing plants is an attractive alternative. There are a lot of annual plants that can be used as source of lignocellulosic fibers for pulp production. These plants can be processed directly for the pulp industry or after a first treatment carried out by the food industry. In these cases the agricultural wastes produced will be the raw material for pulp and paper production. This alternative is nowadays in use in some developing countries with particular emphasis for the utilization of rice and wheat straw and also sugar cane bagasse. From the last decade, even some traditional wood producers started to stimulate enterprises to use agricultural wastes for cellulose production. Brazil is the eleventh world producer of paper and cardboard and the seventh world producer of cellulosic pulps and it still possesses an incalculable potential for increase of pulp production. In this regard it should be included not only the wood, but also annual plants and agricultural wastes as a source of fibers (GERBER et al., 1999).

The wheat culture is one of the most important agriculture activities worldwide and generates an expressive volume of agricultural residues (ca. 750×10^6 $ton/year$) (ROWELL and YOUNG, 1997). The development of pulping processes for these fast growing plants has to take into account their specific morphological and chemical characteristics. The pulping processes nowadays in operation at industrial scale were developed considering particularly the utilization of wood as raw material and must be adapted for the treatment of non-wood fibers. The low density of these non-wood species and their well spread production areas claim to specific pulping process and small or middle size mills. In this new perspective, the utilization of steam explosion followed of organosolv delignification can contribute to a valorization of the agricultural residues (SCIARAFFIA and MARZETTI, 1988).

The steam explosion (SE) treatment consists basically in a short cooking at high temperature and pressure in saturated steam. Following the cooking, the digester is discharged by a fast decompression. This treatment consists essentially in a thermochemimechanical process in which hydrolytic reactions prevail. The mechanical effects are due to the forces acting in the decompression step which lead to a massive liberation of the fibers (MARCHESSAULT, 1988).

The conditions for the effective use of this process to the treatment of straws and wood should ensure an effective saturation of the lignocellulosic material by the steam. The equipment should allow fast heating and pressurization of the system and be adapted to produce a fast depressurization of the reactor (MARCHESSAULT, 1988).

The main reactions that happen during the process are the cleavage of easily hydrolyzed glycosidic bonds, cleavage of some ether bonds in lignin and cleavage of lignin-carbohydrate linkages (FOCHER, 1988). The treatment occurs with a predominant hemicellulose extraction and preserved the crystalline structure of the cellulosic moieties. The application of this process to hardwood was already reported as appropriate for the production of pulps, which presented good properties for cardboard production (CAPRETTI, 1988). The production of pulps with low residual lignin contents is only reached by complementary delignification processes. In this case, steam explosion is used as a pretreatment to prepare the lignocellulosic material for the following stages of delignification.

In this work, the acetone-water delignification of steam exploded wheat straw. The steam explosion and organosolv treatment were carried out at different experimental conditions in order to evaluate their influence on the yield and chemical composition of the pulps.

1.1. Experimental

The wheat straw was collected from plantations located at Paraná State - Brazil. The straw was cut to 5 *cm* long pieces. Steam explosion was carried out on laboratory scale at the Pilot Unit of FAENQUIL (Lorena, SP, Brazil). The experiments were performed from 7 *g* of wheat straw in the temperature range of 190-210^{o}C and 4 *min* as reaction time. After each steam explosion treatment the pretreated material was washed with hot water, dried at room temperature and weighed. The pretreated samples were submitted to acetone-water delignification at different temperatures (140, 160 and 200^{o}C) for 60 *min*. The delignification was performed in 120 *mL* stainless steel tube-shaped reactors fitted into an oil bath for heating. Each experiment was performed with 2.0 *g* of air dried steam exploded sample and 40.0 *mL* of acetone-water (1:1,v:v) mixture. The residual straw was filtered, washed and dried (ROSA, 1996).

The residual lignin content was determined gravimetrically (Klason lignin-T230-om82 TAPPI method). The sugars were determined by High Performance Liquid Chromatography (HPLC) using procedures described in the literature (ROCHA, 1997).

2. Results and discussion

The association of two different techniques in order to achieve a better performance claims to a complementary behavior between these processes. The production of cellulosic pulps with high cellulose content must be found together with high polyoses and lignin removal. Steam explosion is more selective for polyoses removal and should be complemented with an efficient process for lignin dissolution. The results presented in Table 1 show that the processes employed for wheat straw were not always complementary. The conditions employed in steam explosion were enough to produce high dissolution yields with only 4 *min* reaction times. The similar yields obtained at 200^{o}C and 210^{o}C do not mean a similar chemical composition for the steam exploded wheat straw, as will be showed in the discussion of the organosolv delignification results.

Organosolv delignification of wheat straw can also produce high dissolution rates. The pulp yield obtained at 200^{o}C and 60 *min* reaction time were in the same order of magnitude than that found when steam explosion was performed at higher temperatures (Table 1). The combined use of steam explosion pretreatment and organosolv delignification shows complementary results only for the delignifications performed at low temperature (140^{o}C). The delignification yields obtained at higher temperatures were systematically higher than those obtained from unexploded wheat straw samples. The low performance of the organosolv delignification, when performed with steam-exploded samples can be explained on the light of chemical modifications occurred during steam explosion.

Despite the higher yields obtained in the organosolv delignifications the pretreatment with steam explosion led to lower accumulated yields (Table 1).

The mechanism in organosolv delignification involves the action of acid catalysts and nucleophiles in order to produce the cleavage of ether bonds present in the lignin structure. Organosolv delignifications performed with no external catalyst are efficient only at high temperatures due to production of acetic acid from the acetyl groups present in polyoses. The removal of polyoses is also an important requisite to obtain higher delignification yields. In the steam explosion treatment, the main reactions involve hydrolysis of polyoses and acetyl groups. Although the removal of polyoses bring some advantages to the following delignification step, the decrease in acetyl content reduces the production of acetic acid and decreases the effectiveness in lignin removal.

The chemical composition of wheat straw and wheat straw pulps showed in Table 2 reveals significant differences according to the characteristics of both treatments. The auto-catalyzed organosolv pulping produces high delignification yields only at high temperatures. On the other hand, steam explosion led to an increase in residual lignin contents as consequence of preferential polyoses removal.

Steam explosion temperature (^oC)	Organosolv pulping temperature (^oC)	Steam explosion yield (^oC)	Organo-solv pulping yield (%)	Accumu-lated yield (%)
(*)	140	(*)	97.4	97.4
	160		87.7	87.7
	200		54.6	54.6
190	140	77.6	92.3	71.6
	160		84.9	65.9
	200		57.0	44.2
200	140	59.1	91.7	54.2
	160		87.7	51.8
	200		68.2	40.3
210	140	58.6	85.3	50.0
	160		82.0	48.1
	200		74.0	43.4

* Organosolv pulping performed without the steam explosion pretreatment.

Table 1: Steam explosion and organosolv pulping yields obtained in the treatment of wheat straw. The reaction times in the steam explosion and organosolv treatments were 4 and 60 min, respectively.

The benefits of steam explosion were found until a certain level of acetyl and polyoses removal was reached. Steam explosion performed at higher temperatures produced pulps with higher lignin contents (after the organosolv delignification steps) when compared to the results obtained when organosolv pulping was performed on unexploded samples.

The pretreatment led to an increase in the total amount of extracted lignin in the organosolv pulping as consequence of the low accumulated yields obtained after the combined treatment. This effect was more pronounced when the organosolv pulping was performed at lower temperatures.

3. Conclusions

From the set of experiments described in this work, one can conclude that the best conditions were found in the steam explosion treatment performed at lower temperatures combined with organosolv delignifications carried out at higher temperatures.

The pretreatment carried out using steam explosion led to an increase in the amount of extracted lignin after the organosolv pulping. This effect was more pronounced for the pulping performed at lower temperatures at the organosolv step.

The use of higher temperatures in the steam explosion treatment was more significant considering the amount of removed lignocellulosic components.

Considering the characteristics of both steam explosion and organosolv delignification the addition of an external catalyst in the organosolv step could produce high delignification extent at low temperatures.

Temperature (^0C)		Cellulose	Polyoses	G. Acetyl	Lignin
S. E.*	O. P.*	(%)	(%)	(%)	(%)
(**)	(**)	41.0	26.0	n. d.	22.0
	140	n. d.	n. d.	n. d.	18.5
	160	n. d.	n. d.	n. d.	11.4
	200	n. d.	n. d.	n. d.	8.6
190		46.2	25.5	2.2	24.1
200		54.0	21.5	1.4	24.2
210		60.6	9.7	1.0	27.8
190	140	56.1	17.1	2.5	23.6
190	160	59.4	13.5	3.8	22.9
190	200	74.7	7.4	0.4	9.6
200	140	63.7	13.2	2.2	20.2
200	160	65.6	9.8	1.3	19.7
200	200	72.0	7.0	0.5	9.5
210	140	70.9	6.5	0.9	18.2
210	160	72.2	5.9	1.2	15.7
210	200	73.8	3.8	0.9	12.1

(*) S. E.= steam explosion; O. P. = organosolv pulping
(**) Untreated sample
n. d. = not determined

Table 2: Chemical composition of wheat straw and wheat straw pulps obtained in the steam explosion and/or organosolv pulping treatments. The reaction times in the steam explosion and organosolv treatments were 4 and 60 min, respectively.

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